

A Study of Methods of Mineralogical Analysis
And Their Application to
the Identification of a Chemical Precipitate

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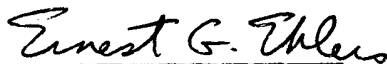
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ABSTRACT. The methods of X-ray powder diffraction, differential thermal analysis, and polarized light microscopy were studied. These methods were applied to the identification of a chemical precipitate formed within a ceramic glaze suspension. The compound was identified as Calcium Diborate Tetrahydrate. The occurrence of this compound indicates the need to study the relationship between composition and useful shelf life of ceramic glaze preparations.

INTRODUCTION

The purpose of this investigation is (1) to study several methods of mineralogical analyses and (2) to apply these methods to the identification of a crystalline substance. The methods of differential thermal analysis (D.T.A.), X-ray powder diffraction, and polarized light microscopy were used to determine the composition of a chemical precipitate that formed within a ceramic glaze suspension. The samples for this analysis were supplied to the investigator by J. Saling (Dept. of Ceramic Engineering, O.S.U.) and E. Ehlers (Dept. of Geology and Mineralogy, O.S.U.)

DESCRIPTION

A sample of ceramic glaze suspension having the composition shown in Figure 1. was prepared by the Ceramic Engineering Department of the Ohio State University. This material was mixed in distilled

<u>w t. %</u>	<u>material</u>
41.5	Buckingham Feldspar (KAlSi_3O_8)
28.8	Potters Flint (SiO_2)
12.3	CaCO_3
7.4	Kentucky Ball Clay #4 ($\text{Al}_4\text{Si}_4\text{O}_{10}\text{OH}_8$)
4.9	BaCO_3
3.1	Boric Acid (H_3BO_3)
2.0	MgCO_3
<u>100.0</u>	Total

Figure 1. Original composition of the ceramic glaze by weight percent.

water and then ball-milled until all particles passed through a 200 mesh screen. The prepared glaze was then placed in a sealed container and stored at room temperature for approximately four years. When opened for use, crystalline masses were found to have precipitated from the glaze (see Figure 2.). The precipitate occurred as spherical aggregates of opaque white crystals having an average diameter of 2.5 centimeters. These aggregates are composed of radiating elongate crystals displaying coxcomb twinning; the surfaces of the aggregates are irregular and contain inclusions. The aggregates are insoluble in water and do not react with hydrochloric acid.

EXPLANATION of METHODS of ANALYSES

Differential Thermal Analysis. This method of analysis is used to record the difference in temperature during uniform heating or cooling between the substance being investigated and an inert reference material. Both samples are placed in an environment that is either heated or cooled at a constant rate and is identical for both samples. The samples are connected by means of differential thermocouples, which record the difference in temperature between the sample and the inert reference material (see Figure 3.). Depending upon the nature of the substance being investigated and the temperature range to which it is subjected, the differential thermal curve obtained will show one or more peaks or depressions, the temperature and shape of which are characteristic of that substance. These thermal depressions represent endothermic reactions and the peaks represent exothermic reactions. Such reactions include phase



Figure 2. Photographs of the crystal aggregates.
Scale is in inches.



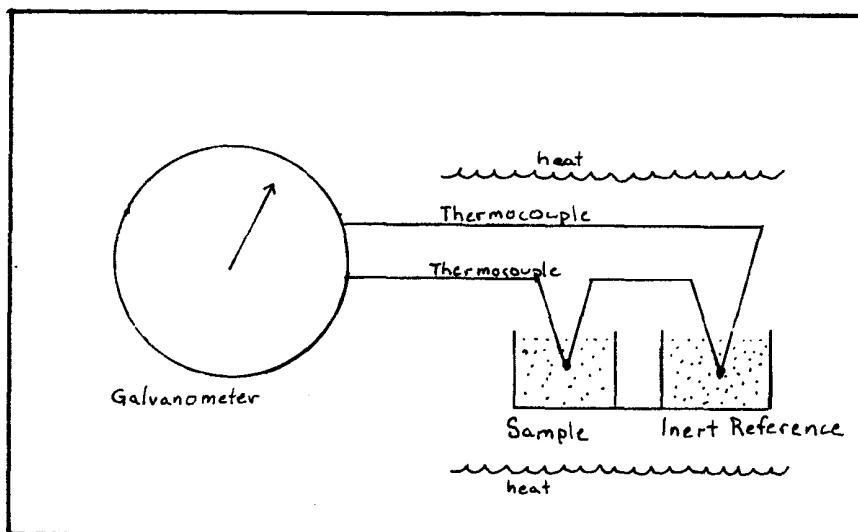


Figure 3. Simplified diagram of differential thermal analysis apparatus.

changes, dehydration, melting and other physical and chemical changes.

During an endothermic reaction, heat supplied by the DTA furnace is absorbed by the reaction of the sample, which therefore has a lower temperature than the inert reference material. This is shown by a downward trend in the DTA curve. At the base of the endothermic depression, the amount of heat absorbed by the reaction is balanced by the heat absorbed to maintain or increase the sample temperature. During the entire endothermic depression, the amount of heat absorbed by the sample is greater than the amount absorbed by the reference material. After the endothermic depression has

leveled out, the amount of heat absorbed by both the sample and the reference material is constant and equal, and the temperature differential again approximates zero. Endothermic depressions are generally caused by dehydration or decarbonation.

During an exothermic reaction, the opposite occurs. The reaction generates heat above that furnished by the DTA furnace. Consequently the sample becomes hotter than the reference material; this is seen as a positive peak on the DTA curve.

For both types of reactions, the apex of the curve represents the point at which the amount of heat either supplied or absorbed by the reaction is equal to the amount of heat absorbed from the DTA furnace. The completion of the reaction is represented by the point where the heating curve of the sample is parallel to that of the reference material.

X-Ray Diffraction. This method of analysis is based on the fact that crystalline substances can diffract incident beams of monochromatic x-rays. If x-rays are targeted at a crystalline substance, the x-rays may be either scattered, transmitted, or absorbed. If the x-ray waves scattered by regularly spaced atoms are in phase, a diffracted beam results. The angle ϕ of the diffracted beam is the glancing angle, and is the complement of the angle of incidence θ . As the angle of incidence and the angle of diffraction are equal, this gives the appearance of a normal reflected ray. Parallel planes of atoms, with interplanar spacing "d", will produce such a beam when the diffracted x-rays from different parallel planes are in phase and thus reinforce each other. For

this to occur, the difference in travel distance between two beams diffracted by different planes of atoms must be equal to an integral multiple of the x-ray wavelength λ . Thus, identical planes of atoms with constant interplanar spacing will diffract x-rays according to the following equation (known as Bragg's Law. See Figure 4.): $n \lambda = 2d \sin \theta$

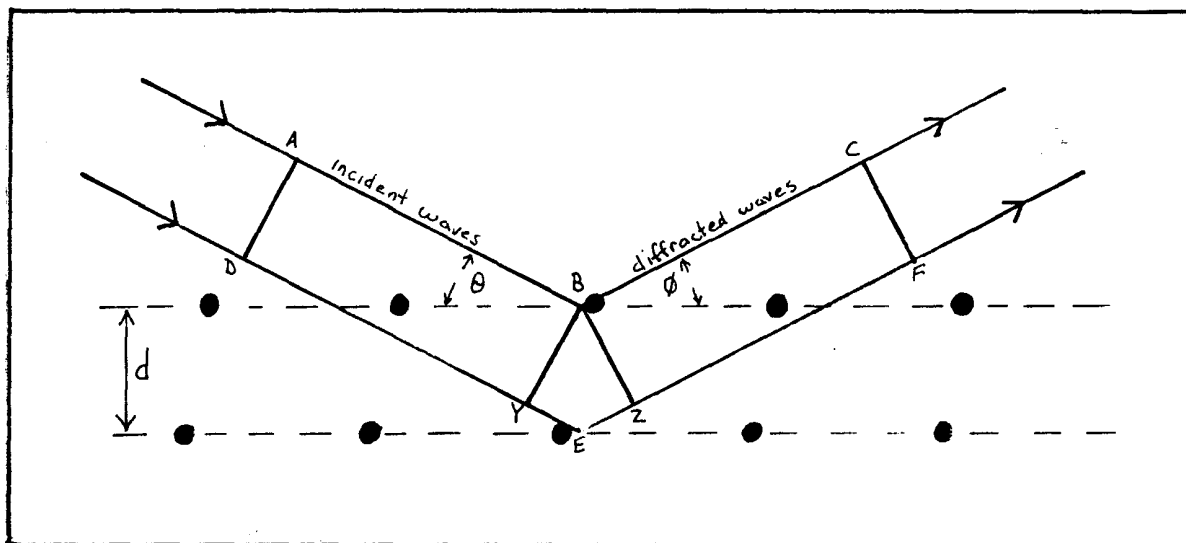


Figure 4. The diffraction of x-rays following Bragg's Law. The path distance differential YEZ is equal to $n \lambda$.

A sample may be analyzed by equipment which produces x-rays of a specific wavelength and measures the intensity of diffracted x-rays as the angle θ is varied. A graphic record may thus be produced which plots θ vs. intensity. Since peaks occur at specific values of θ , corresponding "d" values for these peaks may easily be computed for specific values of λ . A tabulation of "d" values

and corresponding intensities may then be compared to the X-Ray Powder Data File to identify the sample.

Thin Section Study. The standard petrographic thin section consists of a $30_{\mu m}$ thick section of the desired material bonded to a glass slide. The slide is examined under plane polarized light and between crossed polars. The optical properties observed in this manner may aid in the identification of the substance. Important optical properties include index of refraction, optical sign, nature of the optic axes, birefringence, nature of cleavage and crystal habit.

PROCEDURE

Microscopic. A standard petrographic thin section was prepared from a crystal aggregate, such that observations could be made both normal and parallel to the elongate crystals of the aggregate. With crossed polars the material shows a uniform low order gray color, $n_2 - n_1 = 0.003$. No change in color occurred as the microscope stage was rotated. Neither optic sign nor nature of the optic axes could be determined. No cleavage, twinning, or crystal outline other than that of the entire aggregate could be observed. The uniform low order color and lack of observable optical properties indicates a finely crystalline nature, which contrasts with the nature of the aggregates. The material contains numerous fine grained inclusions of quartz, microcline, and carbonate which most likely are remnants of the original suspension.

X-Ray. An x-ray diffraction pattern was obtained with CuK_{α} radiation for a powdered sample of crystal aggregate using a

Phillips XRG 3100 X-Ray Generator. Instrument settings were 35kv., 15ma., 500 c.p.s., T.C. = $\frac{1}{2}$. Initial 2θ was 6° and progressed at $2^\circ 2\theta$ per minute to a maximum value of 67° . Chart speed was $60''/\text{hr}$. (See Figure 5.).

Values of d were determined for all significant peaks. A large number of peaks with intensities near 10 were present. The diffraction patterns corresponding to the microscopically observed included materials were identified by comparison with data from the X-Ray Powder Data File. The composite diffraction pattern was then checked for the presence of diffraction patterns corresponding to the other initial components of the glaze. This allowed only the remaining diffraction pattern corresponding to the crystal aggregate to be considered for further analysis.

The assumption was then made that the x-ray diffraction pattern obtained might not show the true intensities for each peak as a result of preferential orientation or some other factor. The values of d corresponding to the six most intense remaining peaks were recorded. Assuming each of the d values in turn represented the most intense peak for the unknown substance, a comparison of diffraction data was made in the Powder Diffraction File Inorganic Search Manual. A list of all possible compounds falling within the constraints of the diffraction data obtained for the unknown substance and the initial chemical composition of the ceramic glaze was compiled. The X-Ray Powder Data File Card for each of these compounds was then compared to the diffraction pattern obtained for the crystal aggregate. The x-ray data for the aggregates

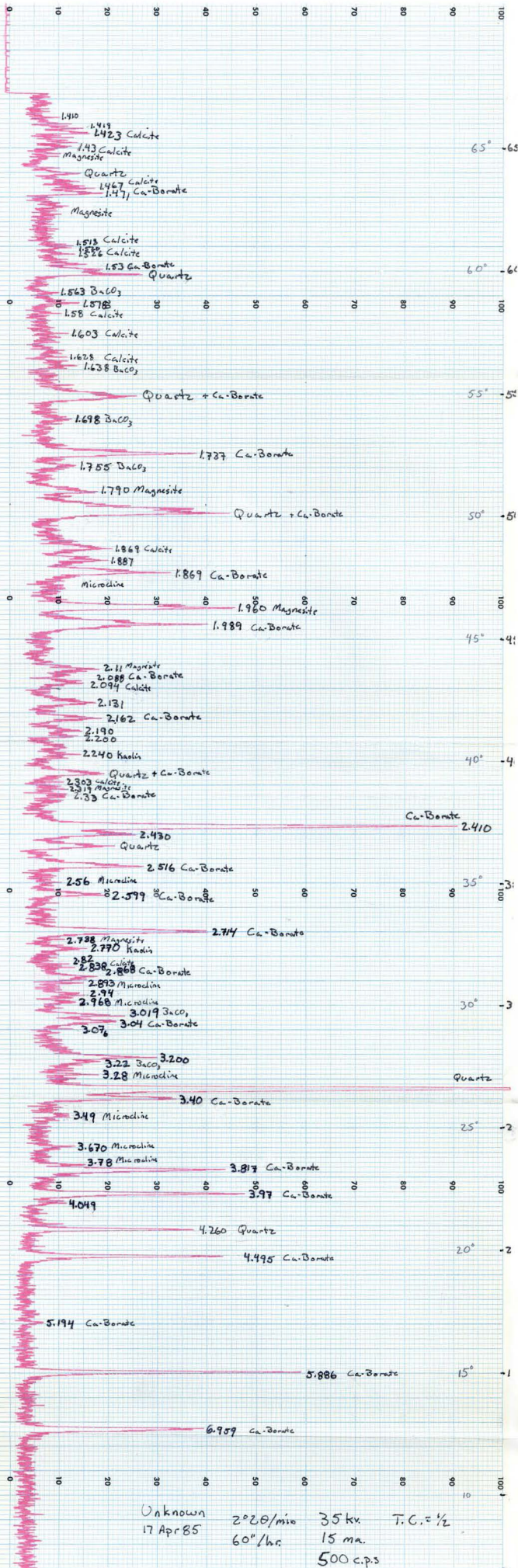


Figure 5.

indicate that they are composed of Calcium Diborate Tetrahydrate ($\text{CaB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$). All but one of the peaks indicated in the X-Ray Powder Data File for this substance were present in the diffraction pattern for the unknown substance. (See Figure 6.)

23-867					23-868				
d	4.48	3.98	3.40	7.03	$\text{CaB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$		$\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$		
1/1 ₁	100	100	100	90	Calcium Borate Hydrate				
Rad. CuK α A 1.5418 Filter Ni Dia. 5.73cm					d A	1/1 ₁	d A	1/1 ₁	
Cutoff 1'1 ₁ Visual					7.03	90	1.81	70	
Ref. Gode and Kuka, Russ. J. Inorg. Chem., 15 603 (1970)					5.86	90	1.73	40	
					5.17	20	1.67	60	
					4.48	100	1.53	30	
					3.98	100	1.47	30	
					3.81	90	1.37	30	
					3.40	100	1.26	30	
					3.05	60	1.16	30	
					2.87	50	1.12	30	
					2.71	100	0.96	20	
					2.58	20			
					2.51	60			
					2.41	100			
					2.34	10			
					2.28	20			
					2.16	40			
					2.06	30			
					1.98	70			
					1.90	50			
					1.88	30			
O assigned because unindexed and insufficient differentiation of intensities. (Ed.)									

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Figure 6. Card number 23-867 from the X-Ray Powder Data File. Data corresponds to that obtained for the crystal aggregate.

Differential Thermal Analysis. A DTA curve for the crystal aggregates was obtained from E. Ehlers (See Figure 7.). A large endothermic peak occurs between 100 C and 200 C. It was assumed that this peak corresponds to a dehydration reaction. Following this assumption, a powdered sample was heated at 200° C for 24 hours and then examined by x-ray diffraction, the desired result being a pattern corresponding to a lower order hydrate or a dehydrated phase of Calcium Diborate in order to confirm the original identification. However, the composite diffraction pattern obtained showed only the diffraction patterns corresponding to the

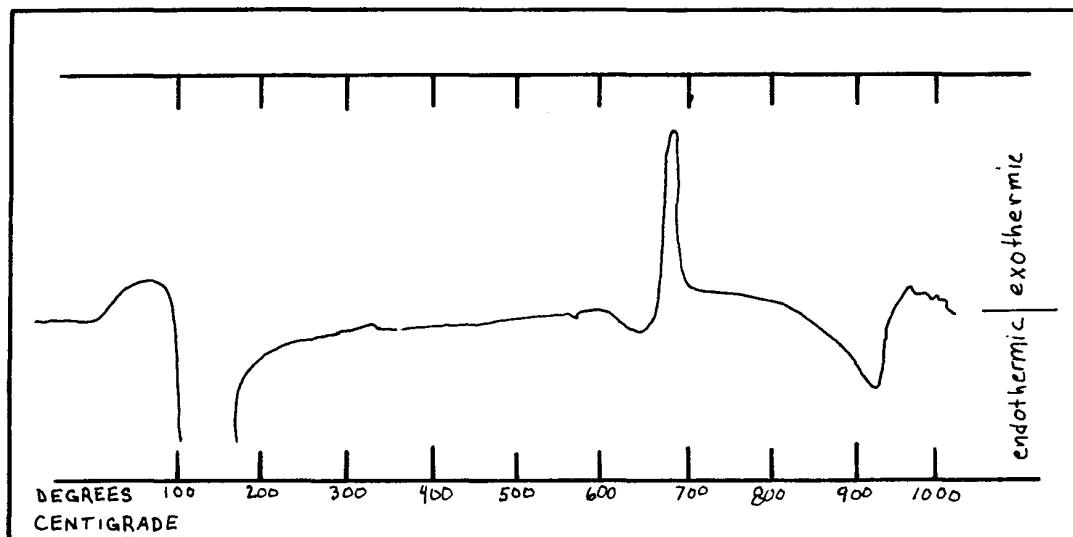
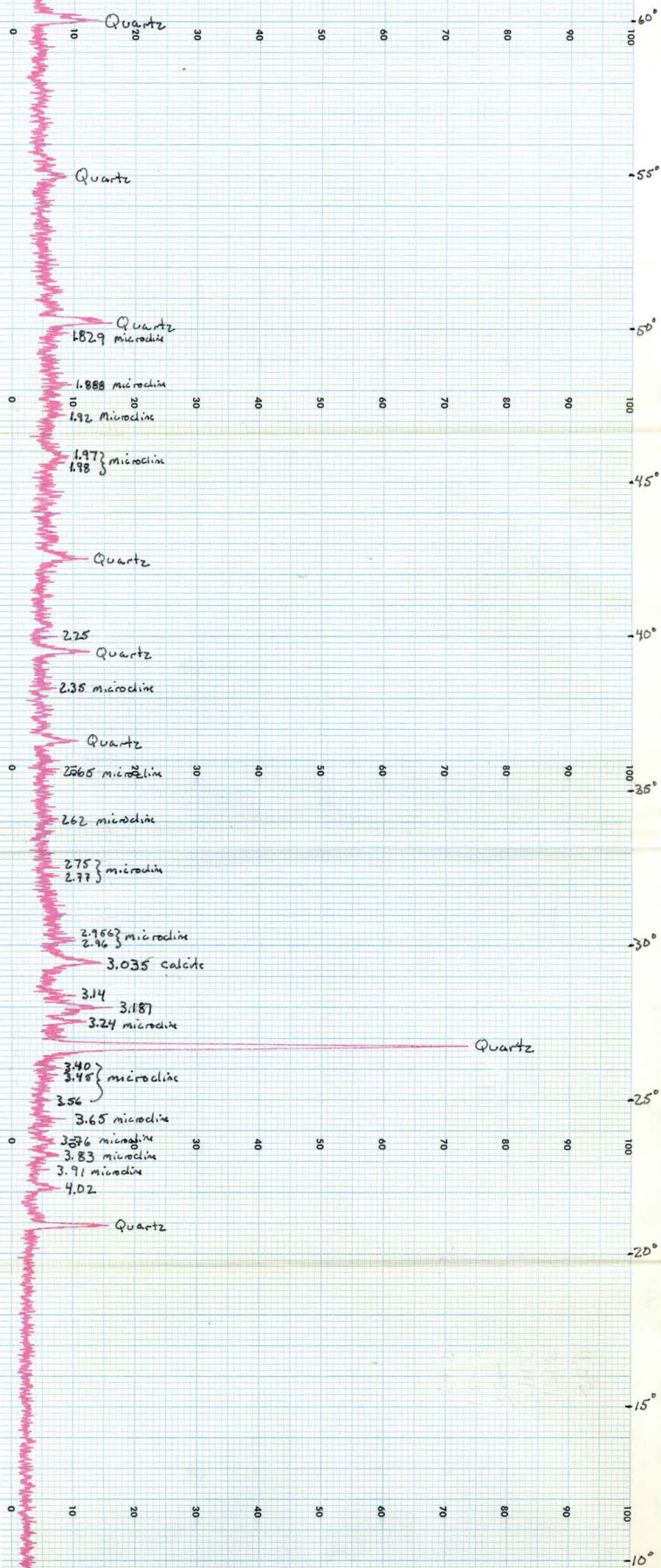


Figure 7. Differential Thermal Analysis curve obtained for the crystalline aggregates.

inclusions observed in thin section of the crystal aggregate (See Figure 8.). This indicates that the endothermic reaction resulted in either an amorphous phase or a product too finely crystalline to diffract x-rays.

DISCUSSION

A wide variety of compounds may be expected to form in aqueous solutions of boric acid and other constituents. A wide variety of compounds are possible, with varying degrees of hydration. Due to the chemical complexity of the system, it is not possible to predict which particular compound will form, and in fact the occurrence of several precipitates can be expected. Calcium Diborate Tetrahydrate and other similar compounds are known to occur in environments similar to that of the ceramic glaze under consideration.



Unknown after 24 hr. at 200°C

10 MAY 85

60"/hr. 35 kv. T.C = 1/2

2° 2θ/min. 15 ma.

500 c.p.s.

Figure 8.

One such compound, $\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$, has a DTA curve very similar to that obtained for the crystal aggregates being analyzed. The DTA curve of the hexahydrate shows an endothermic depression at 90°C which is missing from the DTA curve for the crystal aggregates. Other than this deviation the two curves are similar. If the assumption that this endothermic depression represents the dehydration of the hexahydrate to the tetrahydrate is correct, the differential thermal data obtained for the crystal aggregates reinforces the identification made on the basis of x-ray diffraction data.

All available data indicate that a proper identification has been made. Calcium Diborate Tetrahydrate is known to occur in similar environments to the ceramic glaze being considered; the x-ray diffraction data corresponds to that obtained for the unknown substance; the thermal properties of the unknown substance are similar to those of closely related borate compounds.

APPLICATIONS

Boric acid is a common component in ceramic glaze preparations. This investigation has shown that such preparations can form a variety of precipitates and undergo complex chemical changes. If such preparations are not quickly utilized, the desired properties in the final fired glaze may no longer be attainable. The required firing temperature and final properties of the glaze may vary with time spent on the shelf prior to use.

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